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Short communication

Effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample

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Abstract

The effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample has been investigated. The samples were tested for mercury adsorption using a fixed-bed with a simulated flue gas. The activated fly ash carbon sample has lower mercury capacity than its precursor fly ash carbon (0.23 vs. 1.85 mg/g), although its surface area is around 15 times larger, 863 vs. 53 m^2/g. It was found that oxygen functionality and the presence of halogen species on the surface of fly ash carbons may promote mercury adsorption, while the surface area does not seem to have a significant effect on their mercury capacity.

Keywords: Fly ash carbon; Porosity; Surface functionality; Mercury capture

Coal-fired utility boilers are the largest source of anthropogenic mercury, accounting for 33% of the total mercury emissions [1]. On December 15, 2003 the US Environmental Protection Agency (EPA) proposed to permanently cap and reduce mercury emissions from power plants and when fully implemented in 2018, mercury emissions will be reduced by 69%. The injection of fine carbon adsorbent upstream of the electrostatic precipitator (ESP) or baghouse is a promising technology to control mercury emissions [2]. The mercury capacity, cost and availability of the carbon sorbent play an important role in the feasibility of the proposed carbon injection technology.

Previous work has focused on studying the influence of flue gas complexity [3], carbon amount and particle size [4] on the capacity of the sorbent. Chemical modification of activated carbons with sulfur and halogen elements has been shown to enhance their mercury capacity [5–7]. However, there are only limited studies on the correlation between the porous structure and surface properties of activated carbons and their mercury adsorption capacities. Furthermore, there is even a controversy on the effect of surface functionality of activated carbon sorbents on their mercury adsorption properties [5,8–10]. Some researchers have concluded that oxygen surface complexes are the active sites for Hg^0 capture after conducted a series of studies on various samples with different surface functionalities [5,8,9]. In contrast, other studies claim that oxygen functional groups reduce mercury capture by physisorption and have no effect in the chemisorption regime [10]. Fly ash carbons from pulverized coal combustors (PCC) have fine particle size and on-site availability and have previously been tested as a potential mercury sorbent [4,5]. The purpose of this communication is to describe for the first time the effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample.

The fly ash carbon sample studied here is from a PCC unit burning a high volatile bituminous coal and was collected from the ESP hoppers. This sample has a carbon content of around 58%, which is higher than those reported

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Table 1
Porosity and mercury capacity of the two studied fly ash carbons, and Darco Insul

Sample	Ash Content (%)	S_{BET} (m^2/g)	$V_{0.95}$ (ml/g)	D_a[a] (nm)	Mercury capacity[b] (mg/g)
DEM-PCC1	3.6	53	0.040	1	1.85
AC-PCC1	11.2	863	0.490	2.3	0.23
Darco Insul	–	700	–	–	2.77

[a] Average pore diameter, calculated based on cylinder pore model.
[b] Tested using a fixed bed at 138 °C and the simulated flue gas containing 16% CO_2, 5% O_2, 2000 ppm SO_2, 270 ppm Hg and balanced with nitrogen. The length of exposure is 350 min.

in previous studies that are typically ~15%. However, this work focuses on the utilization of high carbon fly ashes, and therefore, this high carbon content sample was intentionally selected. It is known that the mercury capacity of the inorganic fraction is very low compared to the carbon present in ash [4,11]. Therefore, the sample was subjected to physical separation by a sink/flotation technique using a liquid medium with density 1.6–2.5 g/ml and then followed by an acid digestion step of $HCl/HNO_3/HF$ at 65 °C to produce a carbon rich sample (PCC1-DEM) that was used for the mercury capture studies. The ash content and porosity of the samples were characterized by TGA and nitrogen 77 K isotherms, respectively. These methods are described in more detail elsewhere [12,13]. The ash content and porous structure, including total surface area, pore volume and average pore size (based on the cylinder pore model), for DEM-PCC1 are presented in Table 1. DEM-PCC1 has an ash content of around 3.6% and its surface area and pore volume are 53 m^2/g and 0.04 ml/g, respectively. This suggests that some porosity was generated while in the PCC combustor, where the pores generated are mainly in the mesopore range with an average pore size about 3 nm.

The DEM-PCC1 sample was steam activated at 850 °C for 60 min using a horizontal furnace, as previously described [12]. The porous structure properties of the resultant sample, AC-PCC1, are listed in Table 1. Compared to the parent sample, the one-step steam activation process has successfully increased the surface area and pore volume (53 vs. 863 m^2/g and 0.490 vs. 0.040 ml/g). After activation, the sample has a surface area of 863 m^2/g, which is even higher than that of Darco Insul (700 m^2/g, Table 1), which is a commercial activated carbon used as benchmark for mercury capture studies. Furthermore, its average pore size narrowed down to 2.3 nm compared to 3.0 nm for the parent sample. The mesopore (2–50 nm) size distribution curves of the two samples are shown in Fig. 1. For the DEM-PCC1 sample, most of the mesopores are around 4.0 nm, similar to other activated fly ash carbons [12] and activated carbon fibers [13]. However, for the activated sample, AC-PCC1, in addition to the main peak at around 4.0 nm, another peak around 2.0 nm is observed, indicating that some small mesopores have been generated during the activation process.

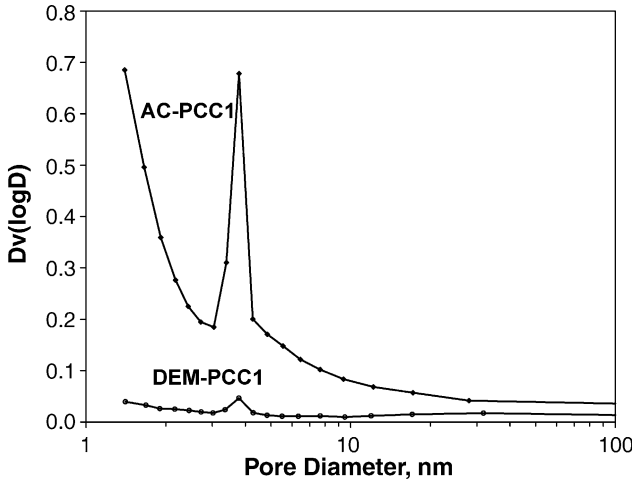

Fig. 1. Mesopore size distribution of the studied fly ash carbon samples.

The fly ash carbon and its activated counterpart were tested for mercury adsorption using a fixed-bed with a simulated flue gas at 138 °C. A detailed description of the mercury capacity test protocol used in this work can be found elsewhere [5]. This simulated flue gas used in the study contained 16 vol.% CO_2, 5 vol.% O_2, 2000 ppm vol. SO_2, 270 ppm vol. Hg and is balanced with nitrogen. The length of exposure was 350 min. The simulated flue gas used here has higher Hg content than that of typical full-scale units (~1 ppb), and does not contain any NO_x. Previous work has shown that NO_x, or more specifically, NO_2, influences the ability of activated carbon to adsorb mercury in fixed bed tests [14]. Nevertheless, the simulated flue gas used here was used to compare the effect of porous structure and surface functionality on a fly ash carbon and its activated counterpart. The samples prior to the mercury adsorption tests were analyzed by a cold vapor atomic absorption spectrophotometer (CVAA) for inherent mercury content. Both samples presented low concentrations of mercury of the order of less than 1 ppm. The mercury capacities of both fly ash carbons were then analyzed as described above and correlated to their porous structure and surface properties. The mercury adsorption tests results are listed in Table 1, where the data obtained under the same conditions for the commercial activated carbon Darco Insul are also presented. The fly ash carbon sample DEM-PCC1 has a mercury capacity as high as 1.85 mg/g, which is comparable to the commercial activated carbon Darco Insul, whose mercury capacity is 2.77 mg/g. Surprisingly, the activated fly ash carbon sample AC-PCC1 has lower mercury capacity than its precursor fly ash carbon DEM-PCC1 (0.23 vs. 1.85 mg/g), although its surface area is around 15 times larger, 863 vs. 53 m^2/g. However, it should be noted that the precursor fly ash carbon has larger pore size than the activated sample (Table 1 and Fig. 1), which suggests that the parent fly ash carbon could have better mass transfer properties than its activated counterpart.

Previous studies on a Thief sorbent, which is a semi-combusted coal extracted from a combustion chamber, have also shown that sorbents with modest surface areas yet exhibit good capacities for mercury from flue gas [15]. Micropores (<2 nm) are the major active sites for most adsorbates, while mesopores act as adsorption sites especially for larger molecules, and also as transportation routes for small adsorbates. In certain cases, the transportation function is more important than the adsorption site function. For instance, in the carbon sorbent injection technology to control mercury emissions, the retention time of carbon in flue gas is very short, and therefore, at most conditions, mass transfer rate is the determining factor and the adsorption of the mercury onto the carbon surface is mass-transfer-limited [16]. Therefore, a carbon sorbent selected for mercury capture should have good mass transfer properties. This is consistent with the data reported here, where, in addition to the total surface area, the pore size also seems to play a role in the mercury capacity of the sorbents. However, the very different mercury capacity of the samples studied here cannot only be ascribed to differences in their porous structures. Other properties, especially surface functionality, are also important to determine their mercury capacity, as described below.

In order to investigate the surface properties of the samples, DEM-PCC1 and AC-PCC1, XPS analyses were conducted using a Kratos Analytical Axis Ultra instrument, and the resultant survey spectra are shown in Fig. 2. For DEM-PCC1, in addition to the two major peaks C 1s and O 1s, there are also two small peaks at 690 and 200 KeV, which are ascribed to F 1s and Cl 2p, respectively. The presence of fluorine and chlorine in the DEM-PC1 sample is probably a result of the acid digestion step, where HCl and HF acids were used. Furthermore, the comparison of the spectra for the two samples also shows that the O 1s peak for DEM-PCC1 is larger than that for AC-PCC1. This indicates that the activation process may have caused the loss of certain oxygen functional groups. In addition, the activation process also removed almost all of F and Cl species from the surface of the sample, as shown by the lack of peaks at 690 and 200 KeV for F 1s and Cl 2p, respectively, for AC-PCC1 (Fig. 2).

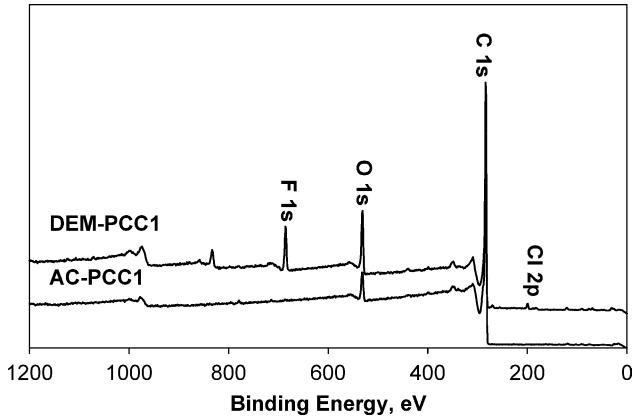

Fig. 2. XPS survey spectra of the studied fly ash carbon samples.

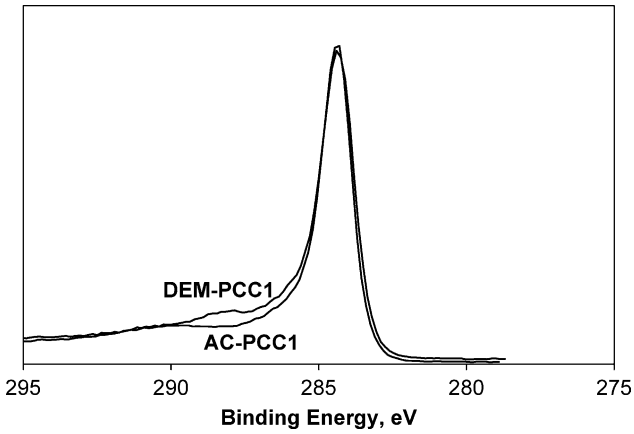

Fig. 3. C 1s spectra of the studied fly ash carbon samples.

The high resolution scan data of O 1s and C 1s peaks for these two samples are shown in Figs. 3 and 4, respectively. In Fig. 3, the C 1s curve of DEM-PCC1 shows a shoulder at higher binding energy besides the main peak at 284 KeV, which is ascribed to oxidized carbon. This corresponds to the O 1s spectrum in Fig. 4, which splits into two peaks at around 532 and 531.5 KeV that are assigned to single bond C–O and double bond C=O, respectively [17].

Previous studies conducted by the authors have focused on different adsorbents for mercury, including activated carbon, and also investigated the effect of several elements including F, Cl, I, S and O on mercury adsorption [5]. EPA studies on the effect of activated carbon surface moisture on low temperature mercury adsorption indicated that surface oxygen complexes provide the active sites for mercury bonding [8], where possibly lacton and carbonyl groups, are the active sites for Hg^0 capture [9]. However, other published work on

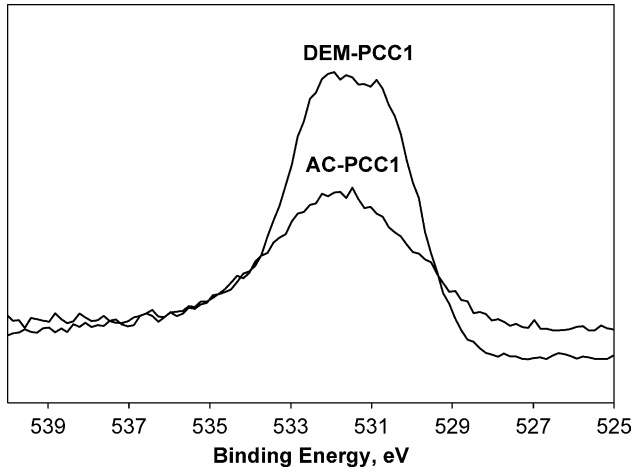

Fig. 4. O 1s spectra of the studied fly ash carbon samples.

the impact of surface heterogeneity on mercury uptake by carbonaceous sorbents under ultra high vacuum and atmospheric pressure concluded that in physisorption regime, oxygen functional groups decrease mercury adsorption due to their blocking of access for mercury to micropores, while in chemisorption regime, no significant impact of oxygen functionalities was observed [10]. The data discussed here supports the claim that the oxygen functionality and the presence of halogen species on the surface of fly ash carbons may promote mercury adsorption, while the surface area does not seem to have a significant impact on their mercury capacity (Table 1). Moreover, it has previously been reported that pre-treating activated carbon with HCl leads to higher capacity for Hg^0 adsorption in fixed bed capture tests [18]. Based on the above data, fly ash carbons from coal-fired power plant have the potential to capture mercury if they have mesoporous structure, and oxygen and halogen functional groups. It has been recently postulated that carbon sorbents have independent reaction sites that comprise at least an oxidation site and also a binding site for the oxidized Hg [19]. Although, this work cannot differentiate between the effect of oxygen functional groups, halogen species, and carbon sites, further studies on the modification of the surface properties of fly ash carbons and their mercury adsorption properties are under way to ascertain the effect of oxygen functionalities, halogen species and carbon sites.

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References

[1] US EPA, A study of hazardous air pollutant emissions from electric utility steam generator units; Final Report to Congress; EPA-453/R-98-004a, 1998.
[2] Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal DL, Benson SA. Fuel Process Technol 2003;82:89.
[3] Carey TR, Hargrove Jr OW, Richardson CF, Chang R, Meserole FB. J Air Waste Manage Assoc 1998;48:1166.
[4] Serre SD, Silcox GD. Ind Eng Chem Res 2000;39:1723.
[5] Granite EJ, Pennline HW, Hargis RA. Ind Eng Chem Res 2000;39:1020.
[6] Korpiel JA, Vidic RD. Environ Sci Technol 1997;31:2319.
[7] Vidic RD, Siler DP. Carbon 2001;39:3.
[8] Li YH, Lee CW, Gullet BK. Carbon 2002;40:65.
[9] Li YH, Lee CW, Gullet BK. Fuel 2003;82:451.
[10] Kwon S, Borguet E, Vidic RD. Environ Sci Technol 2002;36:4162.
[11] Hassett DJ, Eylands KE. Fuel 1999;78:243.
[12] Zhang Y, Lu Z, Maroto-Valer MM, Andrésen JM, Schobert HH. Energy Fuels 2003;17(2):369.
[13] Zhang Y, Wang M, He F, Zhang B. J Mater Sci 1997;32:6009.
[14] Laumb JD, Benson SA, Olson EA. Fuel Process Technol 2004;85:577.
[15] Pennline HW, Granite EJ, Freeman MC, Hargis RA, O'Dowd WJ. US Patent: 6, 521, 021.
[16] Sjostrom S, Ebner T, Ley T, Slye R, Richardson C, Machalek T, Richardson M, Chang RJ. Air Waste Manage Assoc 2002;52:902.
[17] Wang Y, Viswanathan H, Audi AA, Sherwood PMA. Chem Mater 2000;12:1100.
[18] Ghorishi SB, Keeney RM, Serre SD, Gullett BK, Jozewicz WS. Environ Sci Technol 2002;36(20):4454.
[19] Olson ES, Dunham GE, Sharma RK, Miller SJ. Prepr Pap—Am Chem Soc, Div Fuel Chem 2000;45(4):886.